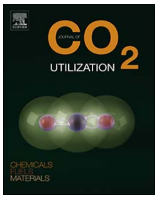
Journal of CO_2 Utilization 22 (2017) 355–373

Contents lists available at ScienceDirect

Journal of CO_2 Utilization

journal homepage: www.elsevier.com/locate/jcou



Multi-objective optimization of combined synthesis gas reforming technologies

J.D. Medrano-García, R. Ruiz-Femenia*, J.A. Caballero

Institute of Chemical Processes Engineering, University of Alicante, Ap. Correos 99, E- 03080, Alicante, Spain

ARTICLE INFO

Keywords:
CO_2 utilization
Synthesis gas
Methane reforming
Superstructure decision making
Multi-objective optimization

ABSTRACT

Synthesis gas (syngas) is a mixture of H_2, CO and occasionally CO_2, whose main application is as a building block of chemical compounds. The desired product dictates the syngas characteristics, which are also affected by the employed syngas synthesis technology. In this work, we study the process of producing syngas under desired specifications while consuming CO_2 in the synthesis. We propose a superstructure that includes seven reforming technologies for the syngas production, as well as a variety of auxiliary units to control the final composition of the syngas. Each potential solution is assessed, in terms of the economic and environmental performance, by the Total Annualized Cost (TAC) and the Global Warming Potential (GWP) indicator. As the problem statement involves discrete decision, we use disjunctions to model the system. The resulting MINLP multi-objective problem is solved by the epsilon constraint method. Results show that at low syngas H_2/CO ratios and pressures, dry methane reforming (DMR) is capable of net consuming CO_2. Partial Oxidation (POX) is the technology that exhibits the minimum TAC, although shows the maximum value for the GWP. Synergistic combination of two processes allows reducing the cost and CO_2-equivalent emissions through the pairing of DMR and bi-reforming (BR) and BR with steam methane reforming (SMR). Furthermore, increasing the CO_2 content in the syngas at a fixed $(H_2 - CO_2)/(CO + CO_2)$ ratio proves that TAC and GWP decrease as the CO_2/CO ratio increases.

1. Introduction

Carbon dioxide has been a matter of concern for the last decades. Its continuous and increasing emission, which is almost guaranteed in any industrial process involving a chemical combustion, must be controlled due to CO_2 being one of the main greenhouse agents originating global warming [1]. In view of this situation, the imperious need to reduce these emissions has been a fact for a long time. The use of low carbon content fuels, improving energy efficiency, the development of new and cleaner technologies or the increasing implementation of renewable energy sources are, amongst other, different approaches made to palliate the problem [2].

Synthesis gas (syngas) is a mixture of gases, mainly formed by hydrogen and carbon monoxide, although carbon dioxide might be also present depending on the application. Syngas can be produced by gasification or reforming of virtually any hydrocarbon source [3] and a reforming agent, like steam, oxygen, carbon dioxide or mixtures of them. Using methane as the carbon source and depending on the reforming agent or mixture of them used, syngas reforming technologies are divided into (Fig. 1): steam methane reforming (SMR), partial oxidation (POX), auto thermal reforming (ATR), combined reforming (CR), dry methane reforming (DMR), bi-reforming (BR), tri-reforming (TR). ATR of natural gas was first introduced by Haldor-Topsoe [4,5] and is also the preferred reforming technology of Sasol [6,7], Air Liquid [8], John Matthey Process Technologies [9] and BP [10] when reforming methane. On the other hand, POX is used by Linde, one of the major contractors of this technology world-wide, which operates the largest plant with natural gas charge (200,000 Nm^3/h of syngas) [11,12]. CR is also used as an alternative by Haldor-Topsoe [5] and Linde [11] among others, although at a lesser extent than the previous two technologies. SMR is the preferred technology when high hydrogen content syngas is required or hydrogen is desired as a byproduct [13].

The "quality" of the syngas changes in each process. This property can be measured with the stoichiometric number also known as *M*, which general formula is:

$$M = \frac{F_{H_2} - F_{CO_2}}{F_{CO} + F_{CO_2}} \tag{1}$$

where F_i is the molar flow (or partial pressure, concentration, etc.) in the syngas. The desired value of *M* is not set in stone, since depending

---

Abbreviations: ASU, air separation unit; ATR, auto thermal reforming; BR, bi-reforming; CR, combined reforming; DMR, dry methane reforming; GWP, Global Warming Potential; HI, heat integration; LCIA, Life Cycle Impact Assessment; POX, partial oxidation; PSA, pressure swing adsorption; SMR, steam methane reforming; STAC, specific total annualized cost; TAC, total annualized cost; TR, tri-reforming; WGS, water gas shift

* Corresponding author.

E-mail address: ruben.ruiz@ua.es (R. Ruiz-Femenia).

http://dx.doi.org/10.1016/j.jcou.2017.09.019
Received 13 July 2017; Received in revised form 19 September 2017; Accepted 25 September 2017

Nomenclature

Indices

i	Syngas processes: SMR, POX, ATR, CR, DMR, BR, TR
j	Components: methane, steam/water, O_2, CO_2, CO, H_2
k	Syngas process units: compressor, exchanger/heater/cooler, reformer reactor
m	Post processing units: absorber1, WGS reactor, bypass1, flash, PSA, compressor, bypass2, absorber2, bypass3
u	Utilities: natural gas, cooling water, power

Parameters

AF	Annualization factor
B_k^1	Bare module parameter 1 of unit k
B_k^2	Bare module parameter 2 of unit k
c_{ik}^f	Fixed cost of unit k in process i [\$]
c_{ik}^v	Variable cost of unit k in process i [\$/capacity units]
c_f^m	Fixed cost of auxiliary unit m [\$]
c_v^m	Variable cost of auxiliary unit m [\$/capacity units]
F_{ik}^P	Pressure factor of unit k
F_k^M	Material factor of unit k
$F_{\max}$	Upper flowrate limit [kmol/h]
IR	Fractional interest rate per year
K_{eq}	Equilibrium constant for WGS reaction
M	Stoichiometric syngas number
nsp	Maximum number of existing syngas processes
P_i	Operating pressure in process i [bar]
$P_{\max}$	Upper pressure limit [bar]
P_{syngas}	Target pressure of the final syngas [bar]
T_{feed}	Temperature of the stream fed to a compressor [K]
t_h	Operating hours per year [h]
T_i	Temperature of the stream leaving process i fed its compressor [K]
V_{abs1}	Volume of absorber column 1
V_{abs2}	Volume of absorber column 2
β_{iu}	Cost of utility u in process i [\$/kmol methane fed]
χ_{ij}	Conversion for component j in process i [kmol j/kmol methane fed]
δ_j	Cost of raw material j [\$/kmol]
ε	Multiobjective optimization epsilon parameter
$\underline{\varepsilon}$	Lower bound of multiobjective optimization epsilon parameter
$\bar{\varepsilon}$	Upper bound of multiobjective optimization epsilon parameter
ϕ_j	GWP associated to raw material j [kg CO_2-eq/kmol j]
φ_{iu}	GWP associated to utility u in process i [kg CO_2-eq/kmol methane fed]

Variables

cap_i	Capital cost of process i [\$]
cap_m	Capital cost of auxiliary unit m [\$]
$cost_i$	Total cost of process i [\$]
$cost_m$	Total cost of auxiliary unit m [\$]
$emission_i$	Total GWP of process i [kg CO_2-eq]
$emission_m$	Total GWP of auxiliary unit m[kg CO_2-eq]
F_{abs}	Absorbed CO_2 flowrate [kmol/h]
F_{H_2}	Hydrogen flowrate separated in the PSA unit [kmol/h]
F_{ij}	Outlet molar flowrate of component j in process i [kmol/h]
F_{ij}^0	Inlet molar flowrate of component j in process i [kmol/h]
$F_j^{recycle}$	Component $j$recycled flowrate to the exist of the syngas processes [kmol/h]
$F_j^{m,in}$	Inlet flowrate of component j to unit m [kmol/h]
$F_j^{m,out}$	Outlet flowrate of component j to unit m [kmol/h]
op_i	Operating cost of process i [\$]
op_m	Operating cost of auxiliary unit m [\$]
P_i^{out}	Outlet pressure of compressor i [bar]
P_{mix}	Pressure after the stream convergence before the WGS/absorber selection [bar]
$power_i^{comp}$	Electricity consumption of compressor after process i [kW]
$power_m$	Electricity consumption of auxiliary unit m [kW]
raw_i	Raw material cost of process of process i [\$]
y_i	Binary variable associated to the existence of process i
y_i^{comp}	Binary variable associated to the existence the compressor after process i
y_m	Binary variable associated to the existence of auxiliary unit m
Y_i	Boolean variable associated to the existence of process i
Y_i^{comp}	Boolean variable associated to the existence the compressor after process i
Y_m	Boolean variable associated to the existence of auxiliary unit m
ΔP_i	Increase in pressure achieved in compressor i [bar]

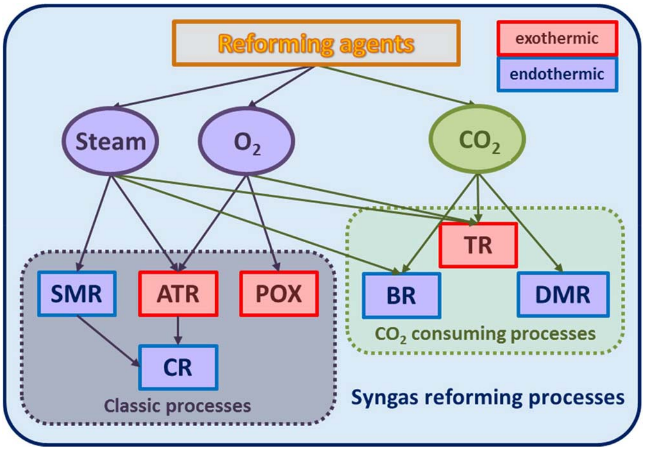


Fig. 1. Syngas reforming technologies sorted by reforming agents employed.

on the application it can range from almost zero (mainly CO when there is no CO_2) to high values in order to get pure hydrogen (Fig. 2).

Reforming technologies are cost intensive due to the high temperatures required to carry out the reactions (see Section 2). In addition, the massive use of fuel significantly increases emissions while operating the plant. However, these aspects led to the development of the combined reforming technology [14], which uses SMR and ATR in a single process. This combination allows not only gaining more control over the H_2/CO ratio but also using the exothermicity of ATR to partially fuel the SMR reactor. Several authors have studied other combinations of these technologies. Lim et al. [15] proposed a combination of SMR and DMR in which the latter used the CO_2 produced in the former to increase the syngas production, successfully mitigating both cost and emissions. Farniaei et al. thermally coupled the exothermic TR with SMR and DR [16,17] in concentric reactors, producing two different composition syngas flows (mixable to achieve a specific ratio) while reducing the energy consumption.

In this work, we propose a superstructure to manufacture syngas with a specific composition. This superstructure includes classic (i.e., non-CO_2 consuming) and CO_2 consuming reforming processes as well as a posttreatment section in which the syngas composition is further